On the participation of crystalline hydrate water in the solid phase $Mn_2P_2O_7 \cdot 5H_2O$ hydrolysis

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Dehydration of hydrated salts is often accompanied by their solid-phase hydrolysis. It causes significant complications of thermal and structural transformations of crystalline hydrates, in particular the phenomenon of polycondensation of phosphate anion. However, it is not insufficiently studied.

The purpose of this work is to establish the sequence of thermal and structural transformations accompanying thermolysis of $Mn_2P_2O_7 \cdot 5H_2O$ and the participation of crystalline hydrate water in its solid phase hydrolysis.

Thermolysis of $Mn_2P_2O_7 \cdot 5H_2O$ was studied in the range of 298–1273 K under dynamic and quasi-isothermal heating conditions (derivatograph Q-1500D). Heat treatment products were obtained at temperatures of thermal effects on DTA curves and identified using methods of analysis: chemical, X-ray phase analysis, infrared spectroscopy.

According to thermoanalytical experiment, the removal of 1.44 moles of H_2O from $Mn_2P_2O_7 \cdot 5H_2O$ (first stage of dehydration) occurs by the molecular mechanism. The main structural motif of the original crystalline hydrate is retained. Structural changes are recorded by removing 3.96 moles of H_2O (second stage of dehydration). Heating $Mn_2P_2O_7 \cdot 5H_2O$ to 463 K results in the formation of a mixture of two solid phases: $Mn_2P_2O_7 \cdot 2H_2O$ (38.2 wt. % in terms of P_2O_5) and X-ray amorphous monophosphate (8.7 wt.%). Its formation is due to the hydrolytic breaking of P–O–P bonds with the participation of crystalline hydrate water.

The composition of the products of $Mn_2P_2O_7 \cdot 5H_2O$ heating to 573 K is the most complex. In addition to mono- (11.5 wt. %) and diphosphate anion (32.1 wt. %), they contain phosphate with higher degree of polycondensation that is triphosphate (4.3 wt.%). Interpretation of the results shows the realization of a dissociative mechanism of water removal, which leads to solid-phase hydrolysis of the salt. The first step of this process is the formation of the groups of P–OH and M–OH type. They are capable to polycondensation at higher temperatures.

Using the maximum degree of polycondensation (n) as a measure of the solid-phase hydrolysis degree, it was found that in case of $Mn_2P_2O_7 \cdot 5H_2O$ thermolysis $n = 3$ that is 2.0–2.5 times lower than in case of $Co_2P_2O_7 \cdot 6H_2O$ thermolysis when $n = 7$. The obtained data are correlating with the energy state of crystalline hydrate water in these diphosphates. The energy of H-bonds in the structure of $Mn_2P_2O_7 \cdot 5H_2O$ is 40 kJ/mol, and in that of $Co_2P_2O_7 \cdot 6H_2O$ it makes 45 kJ/mol. This leads to a stronger phosphate anion polymerization.

The removal of another portion of crystalline hydrate water from $Mn_2P_2O_7 \cdot 5H_2O$ in the range of 573–603 K leads to a simplification of the anionic composition of the thermolysis products. Owing to their solid-state interaction, the final product, anhydrous crystalline diphosphate $Mn_2P_2O_7$, is formed.

The formation of $Mn_2P_2O_7$ takes place by two routes at the same time. The first route involves the classical thermal dehydration of $Mn_2P_2O_7 \cdot 5H_2O$ (it is realized at 70 %). According to the second route, up to 30 % $Mn_2P_2O_7$ is formed as a result of solid-phase hydrolysis of $Mn_2P_2O_7 \cdot 5H_2O$ involving crystalline hydrate water.